Surface crystallography

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Part of the lecture is taken from Wolfgang Rankes LEED-Script

Literature:

G. Ertl, J. Küppers, Low Energy Electrons and Surface Chemistry, VCH, Weinheim (1985).
M. Henzler, W. Göpel, Oberflächenphysik des Festkörpers, Teubner, Stuttgart (1991).
M.A. Van Hove, W.H. Weinberg, C.-M. Chan, Low-Energy Electron Diffraction, Experiment, Theory and Surface Structure Determination, Springer Series in Surface Sciences 6, G. Ertl, R. Gomer eds., Springer, Berlin (1986).
M. Horn-von Hoegen, Zeitschrift für Kristallographie 214 (1999) 1-75.

Content

Bravais lattices

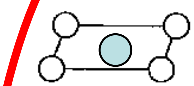
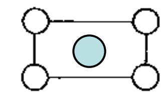
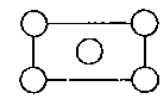
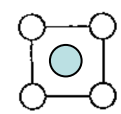
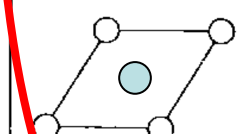
INTERNATIONAL TABLES
FOR
CRYSTALLOGRAPHY

or

International Tables for X-Ray Crystallography, N. F. M. Henry and K. Lonsdale, Eds. (The Kynoch Press, Birmingham, 1969) ,chap. 1.

Bravais lattices

Table 9.1.7.1. *Two-dimensional Bravais lattices*

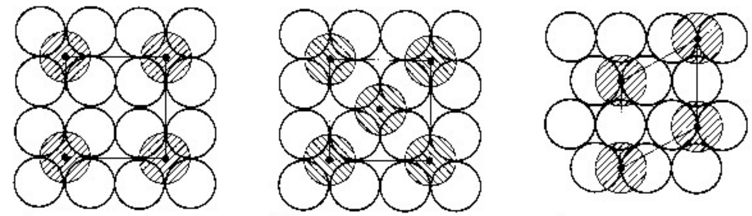
Bravais lattice*	Lattice parameters: Conventional	Lattice parameters: Primitive	Metric tensor: Conventional	Metric tensor: Primitive/transf.†	Metric tensor: Relations of the components	Projections
mp	a, b γ	a, b γ	$\begin{matrix} g_{11} & g_{12} \\ & g_{22} \end{matrix}$	$\begin{matrix} g_{11} & g_{12} \\ & g_{22} \end{matrix}$		
op	a, b $\gamma = 90°$	a, b $\gamma = 90°$	$\begin{matrix} g_{11} & 0 \\ & g_{22} \end{matrix}$	$\begin{matrix} g_{11} & 0 \\ & g_{22} \end{matrix}$		
oc		$a_1 = a_2$ γ		$T(C)$ $\begin{matrix} g'_{11} & g'_{12} \\ & g'_{11} \end{matrix}$	$g'_{11} = \frac{1}{4}(g_{11} + g_{22})$ $g'_{12} = \frac{1}{4}(g_{11} - g_{22})$ $g_{11} = 2(g'_{11} + g'_{12})$ $g_{22} = 2(g'_{11} - g'_{12})$	
tp	$a_1 = a_2$ $\gamma = 90°$	$a_1 = a_2$ $\gamma = 90°$	$\begin{matrix} g_{11} & 0 \\ & g_{11} \end{matrix}$	$\begin{matrix} g_{11} & 0 \\ & g_{11} \end{matrix}$		
hp	$a_1 = a_2$ $\gamma = 120°$	$a_1 = a_2$ $\gamma = 120°$	$\begin{matrix} g_{11} & -\frac{1}{2} g_{11} \\ & g_{11} \end{matrix}$	$\begin{matrix} g_{11} & -\frac{1}{2} g_{11} \\ & g_{11} \end{matrix}$		

* The symbols for Bravais lattices were adopted by the International Union of Crystallography in 1985; *cf.* de Wolff *et al.* (1985).
† $T(C) = \frac{1}{2}(11/\bar{1}1)$.

Structure examples: Overlayers

Overlayer structures

Ertl/Küppers fig. 9.2, p.204



a) p(2x2) b) c(2x2) on square lattice

c) (√3x√3)R30° on hex. lattice

Superstructure nomenclature

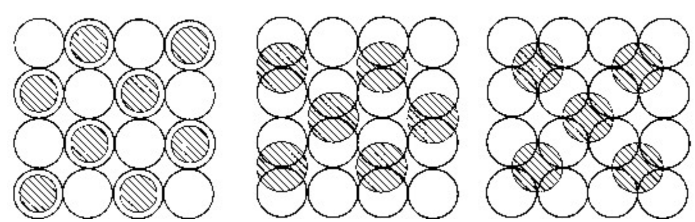
Wood: Simplest in most cases
p or c(n×m)Rϑ°
unit cell vector lengths
$b_1 = n\, a_1$ $b_2 = m\, a_2$
rotation ϑ p=primitive, c=centered

Matrix notation (Park and Madden)
more general

$$\begin{matrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{matrix} \qquad \begin{aligned} \mathbf{b_1} &= m_{11}\, \mathbf{a_1} + m_{12}\, \mathbf{a_2} \\ \mathbf{b_2} &= m_{21}\, \mathbf{a_1} + m_{22}\, \mathbf{a_2} \end{aligned}$$

Wood	(2×2)	[ϑ=0 is omitted]	(√3×√3)R30°
Matrix	$\begin{matrix} 2 & 0 \\ 0 & 2 \end{matrix}$		$\begin{matrix} 1 & 1 \\ 2 & -1 \end{matrix}$

Three possible arrangements yielding c(2x2) structures.
Note: different symmetry but the same LEED pattern!



on top bridge 4-fold hollow

Ertl/Küppers fig. 9.6, p.208

Method: LEED, low energy electron diffraction

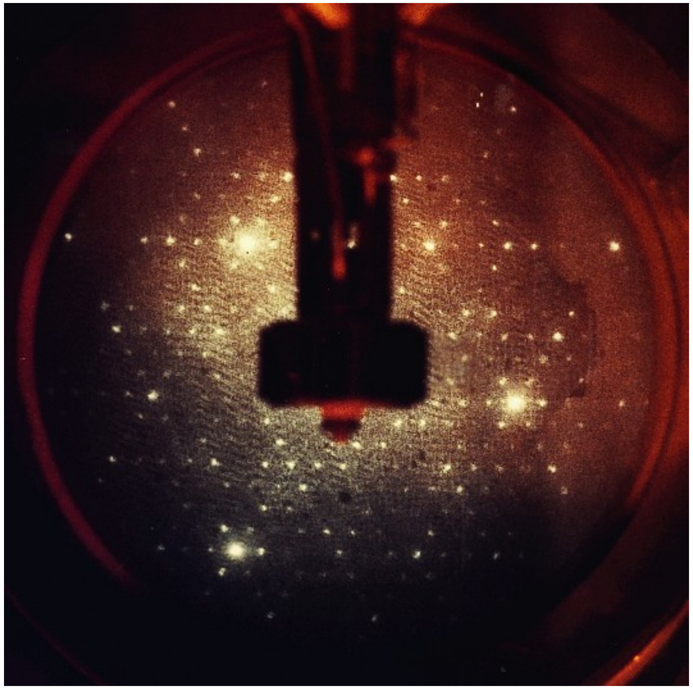
Necessary: Surface science, UHV, p~10^{-10} mbar

De Broglie wavelength: $\lambda = h/(mv)$

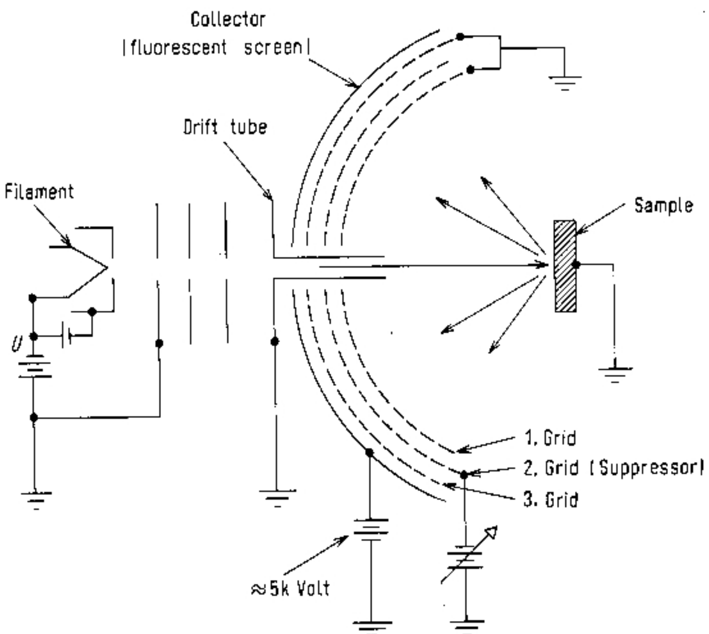
For electrons: $\lambda = \sqrt{150 / E_0}$ E_0 in eV, λ in Å.

For 100 eV-electrons: $\lambda(100) = 1.22$ Å (low energy)

corresponds to atomic dimensions, similar to XRD



Si(111)-(7x7)

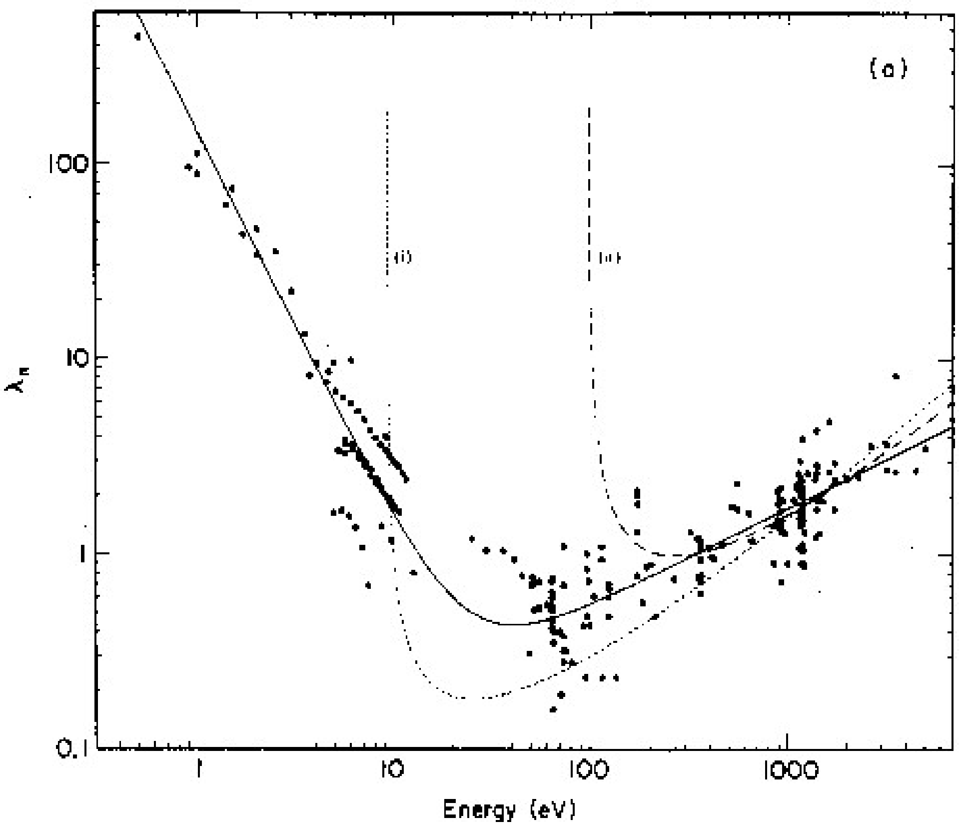


LEED display system

Ertl/Küppers fig. 9.7, p. 210

LEED is surface sensitive

Low energy electrons
interact strongly with matter:
electron mean free path λ_e
is small.
Only e^- scattered from near surface
can leave the surface,
surface sensitive
LEED requires crystalline surfaces



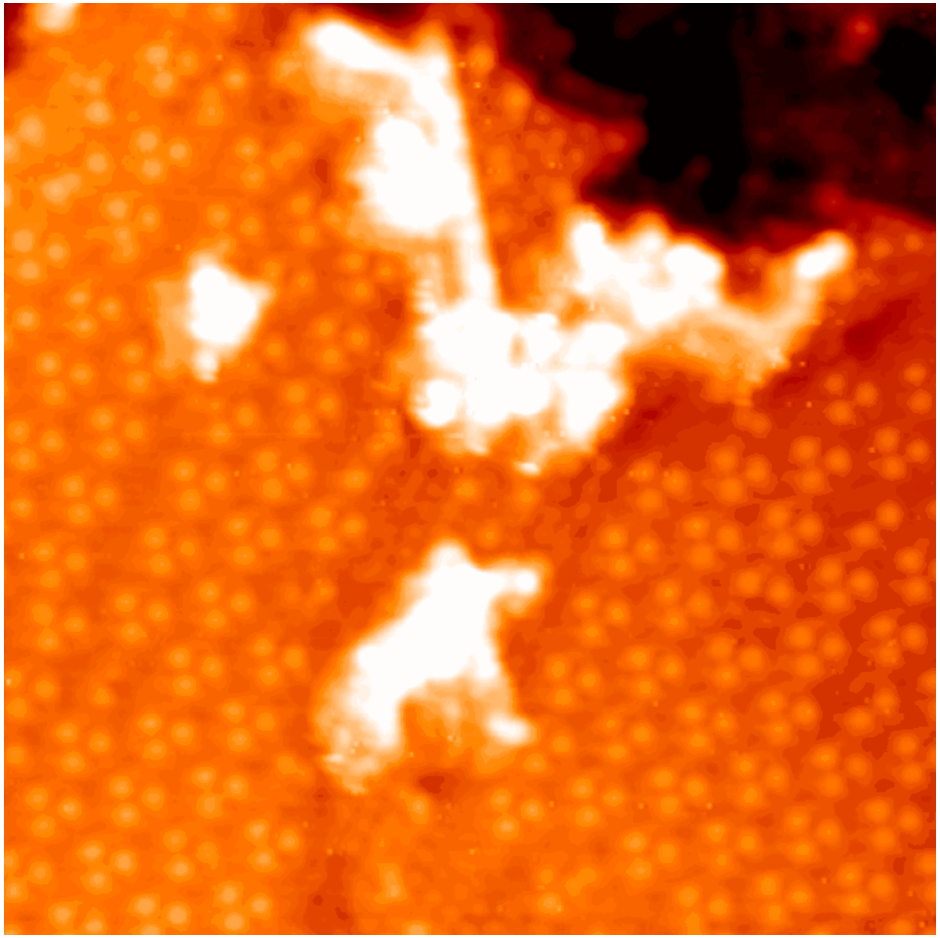
M.P. Seah, W.A. Dench, Surf. Interf. Anal. 1 (1979) 2

The observation of a LEED pattern
does not guarantee that the whole surface is ordered!

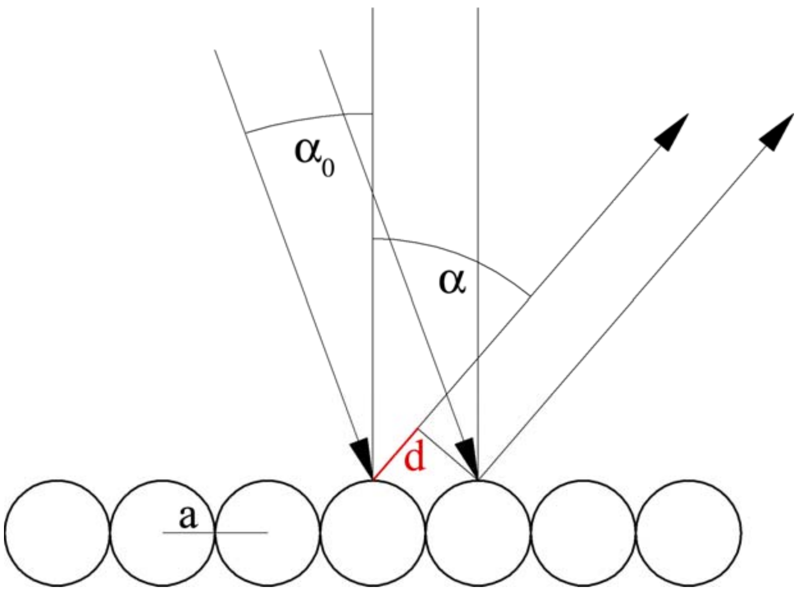
STM

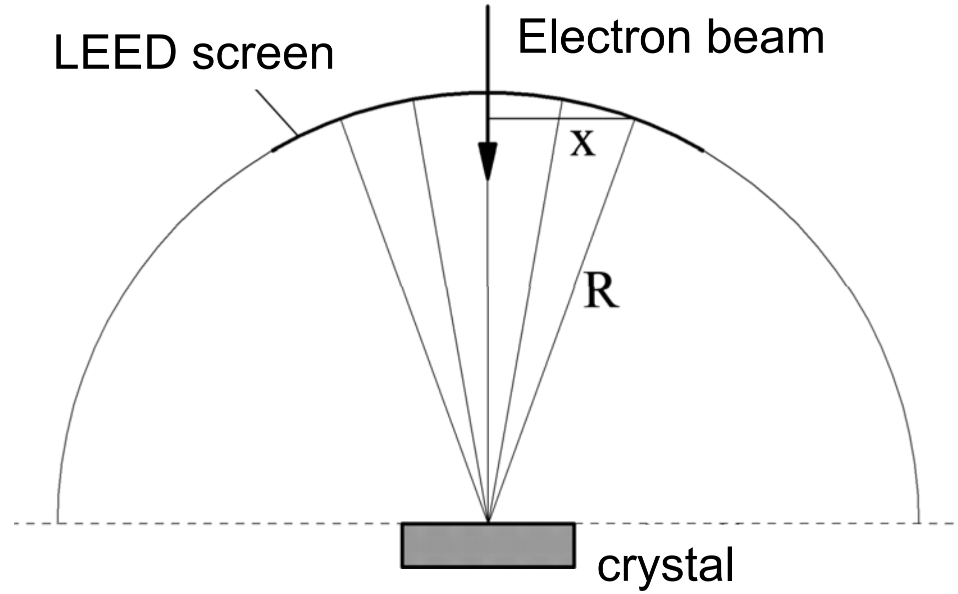
Advantage:
• can look into the unit cell

Disadvantage:
• only local (statistics)



LEED principle in one dimension





$\alpha_0 = 0°$: $$\frac{x}{R} = \sin\alpha = \frac{n\lambda}{a}$$

$$g = n\lambda = d - d_0 = a\left(\sin\alpha - \sin\alpha_0\right)$$

$$\frac{x}{R} = \sin\alpha = \frac{\frac{1}{a}}{\frac{1}{n\lambda}} = \frac{n\frac{1}{a}}{\frac{1}{\lambda}}$$

Useful: Introduction of **reciprocal lattice**

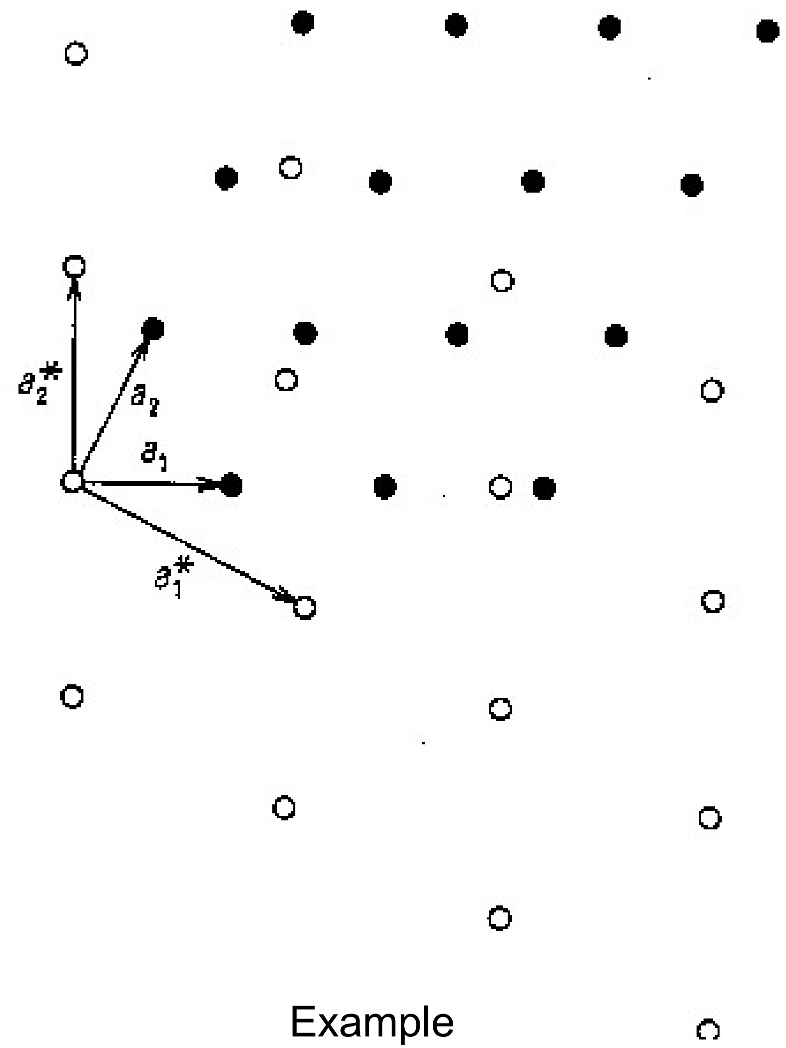
Real lattice vectors **$\mathbf{a}_1$, $\mathbf{a}_2$**

Reciprocal lattice vectors **$\mathbf{a}_1^*$, $\mathbf{a}_2^*$**

Definitions:

$\mathbf{a}_1^*$ perpendicular to **$\mathbf{a}_2$**
$\mathbf{a}_2^*$ perpendicular to **$\mathbf{a}_1$**

$a_1^* = 1/(a_1 \sin \gamma)$
$a_2^* = 1/(a_2 \sin \gamma)$
γ angle between a_1 and a_1

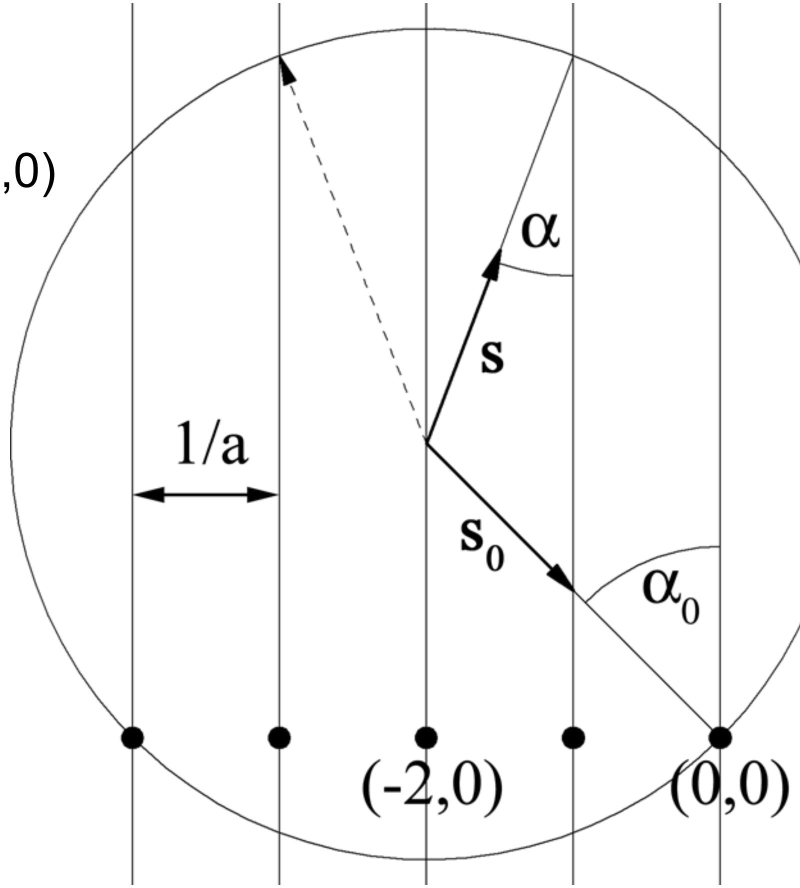


Example

Ertl/Küppers fig. 9.11, p 216

Ewald sphere construction

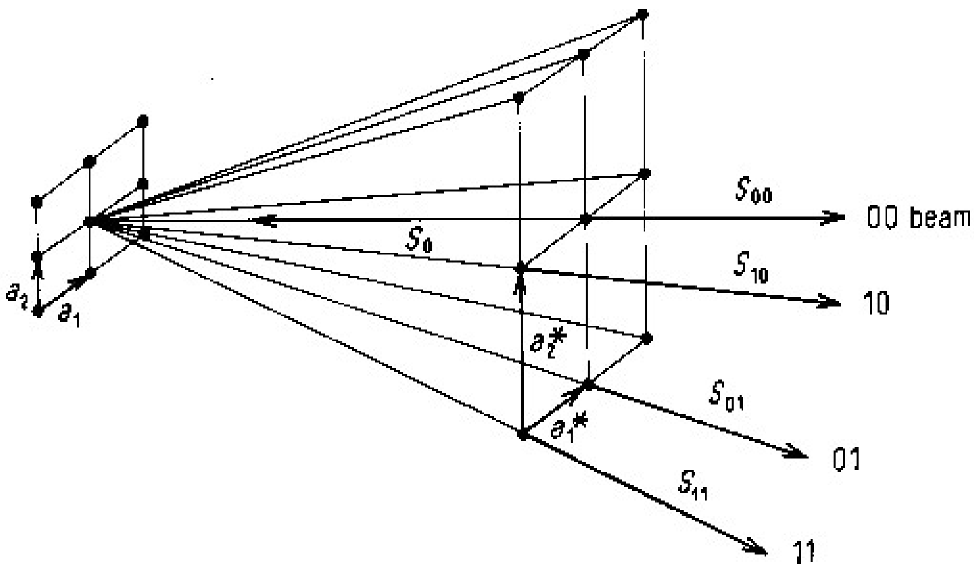
- plot reciprocal lattice (rods)
- plot direction of incident beam (**s_0**) towards origin of the reciprocal space (0,0)
- go from (0,0) $1/\lambda$ along this direction
- make circle (sphere) with radius $1/\lambda$
- direction from circle (sphere) center towards cut with reciprocal lattice rods gives direction of all possible diffraction spots (hk) (here k=0)



Usual arrangement:

Normal incidence, yields a symmetrical diffraction pattern

LEED principle in two dimensions

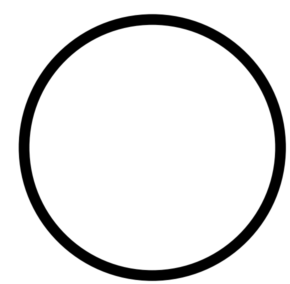


Formation of diffraction pattern

h,k
(order)

Ertl/Küppers fig. 9.12, p. 217

LEED pattern of HOPG?



circle

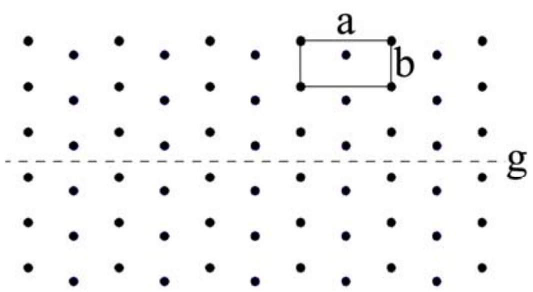
LEED and symmetry

Table 2.2.13.3. *Reflection conditions for the plane groups*

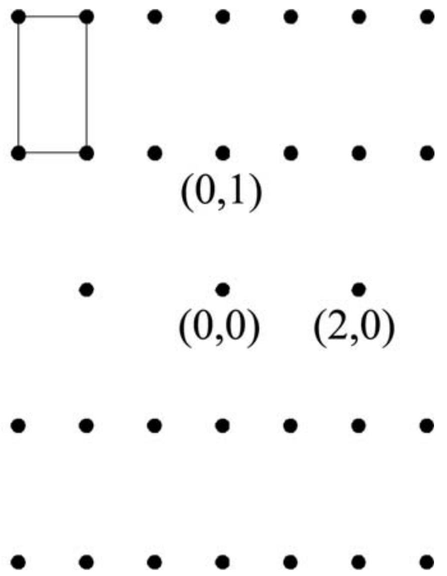
Type of reflections	Reflection condition	Centring type of plane cell; or glide line with glide vector	Coordinate system to which condition applies
hk	None	Primitive p	All systems
	$h+k=2n$	Centred c	Rectangular
	$h-k=3n$	Hexagonally centred h*	Hexagonal
$h0$	$h=2n$	Glide line g normal to b axis; glide vector $\frac{1}{2}\mathbf{a}$	Rectangular, Square
$0k$	$k=2n$	Glide line g normal to a axis; glide vector $\frac{1}{2}\mathbf{b}$	

* For the use of the unconventional h cell see Chapter 1.2.

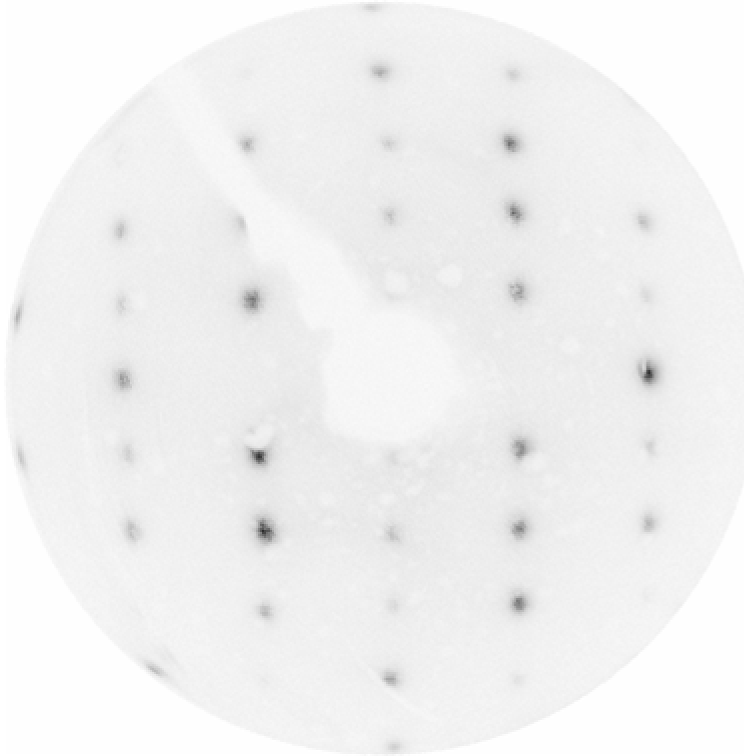
Glide line symmetry and LEED



Real space

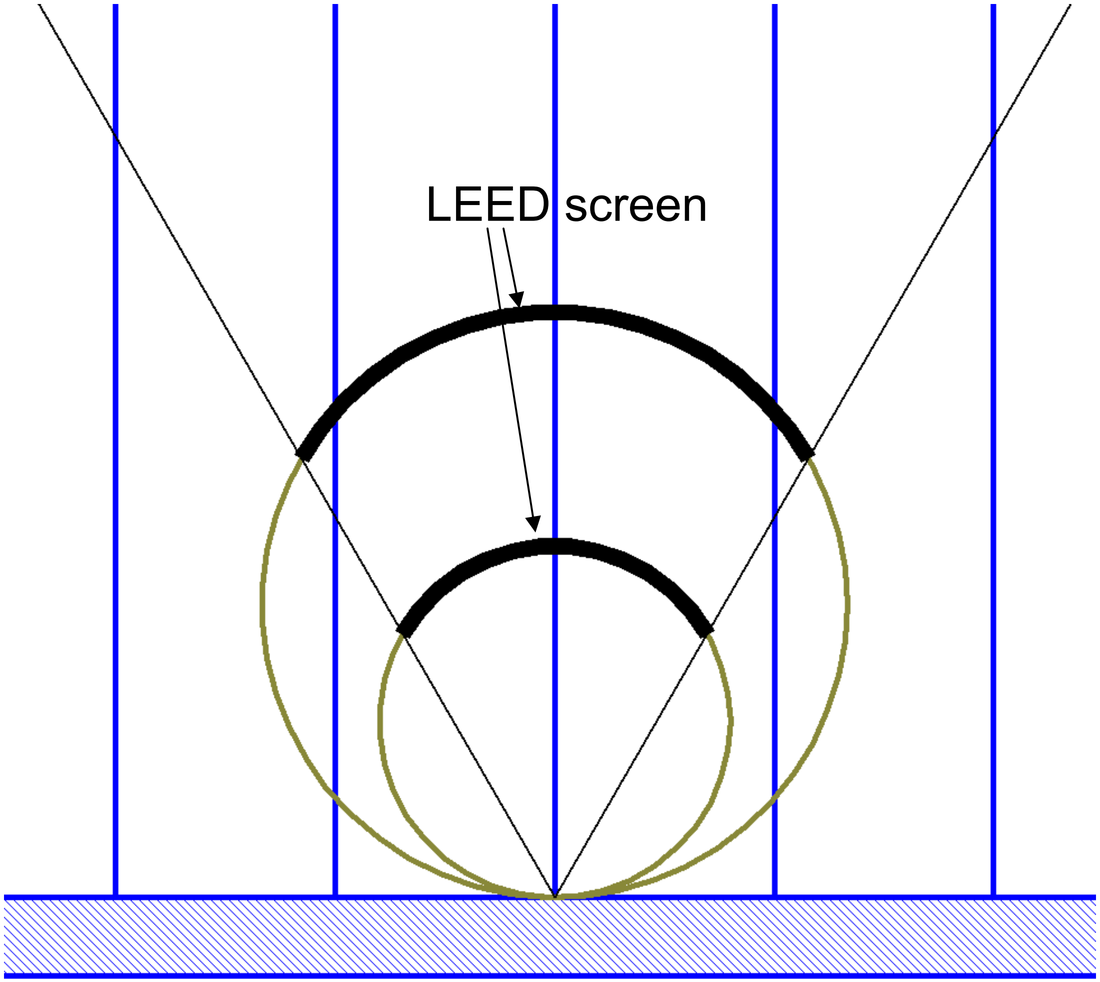


Reciprocal space



LEED pattern

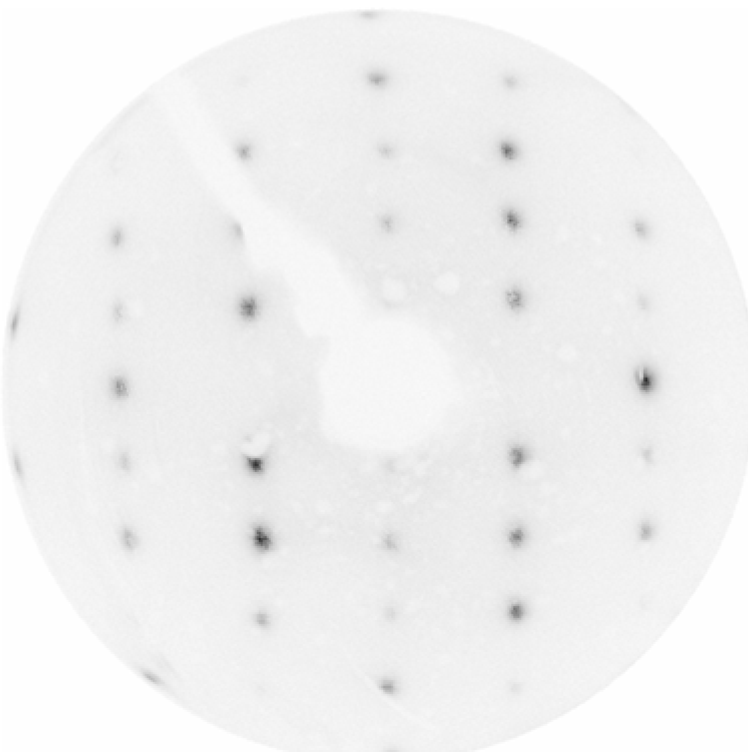
Ewald sphere construction and beam energy

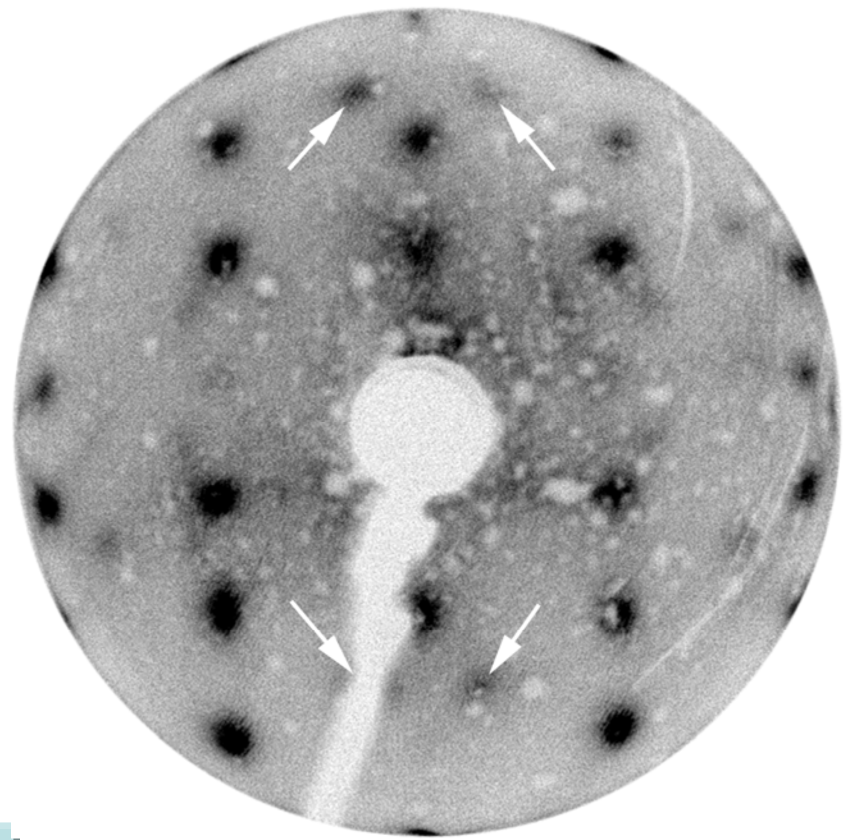


Increasing the beam energy means increasing 1/λ, i.e. a larger Ewald sphere

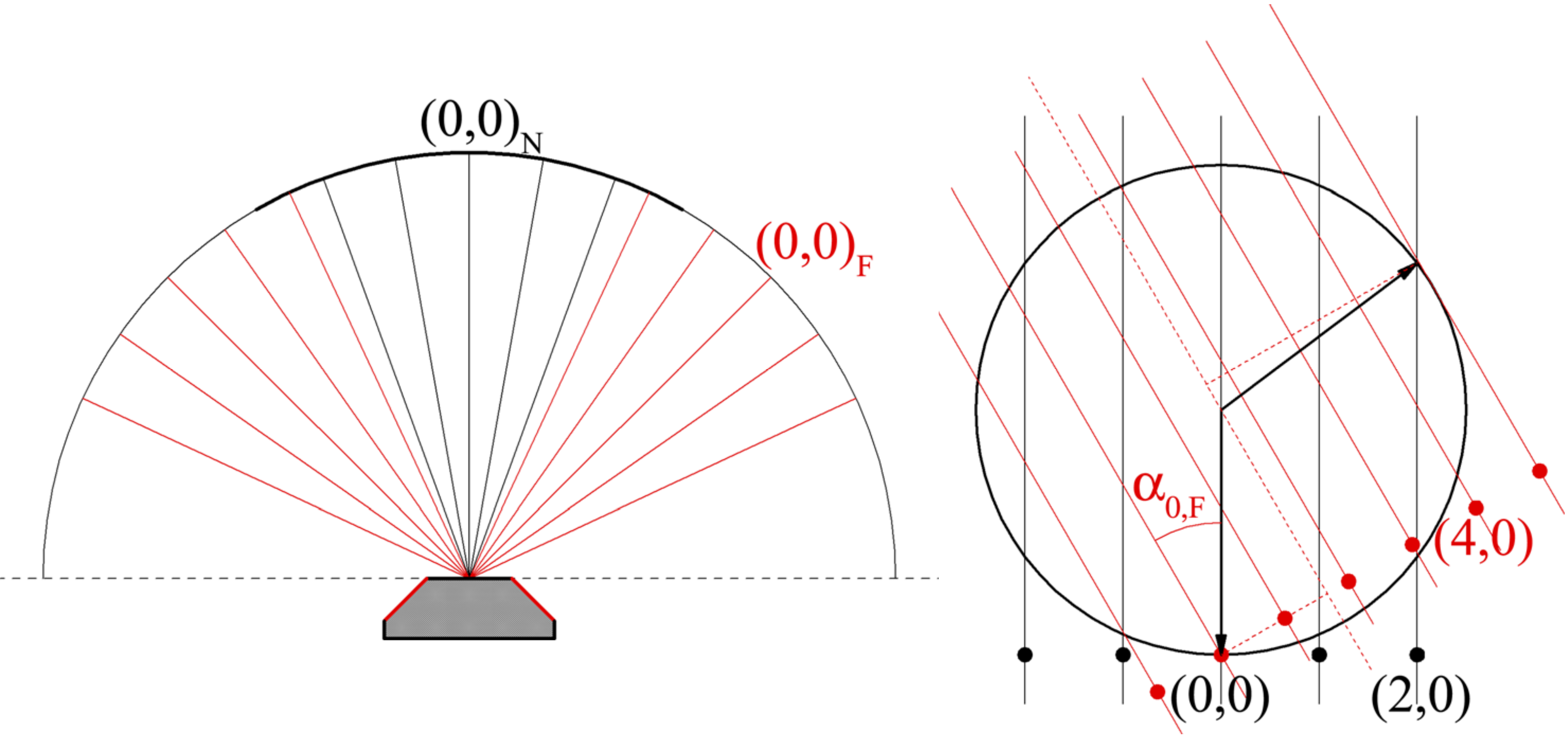
Experiment

- 10 nm TiO_2 deposited on Re(10-10) (known from XPS)
- Surface crystallography? LEED!

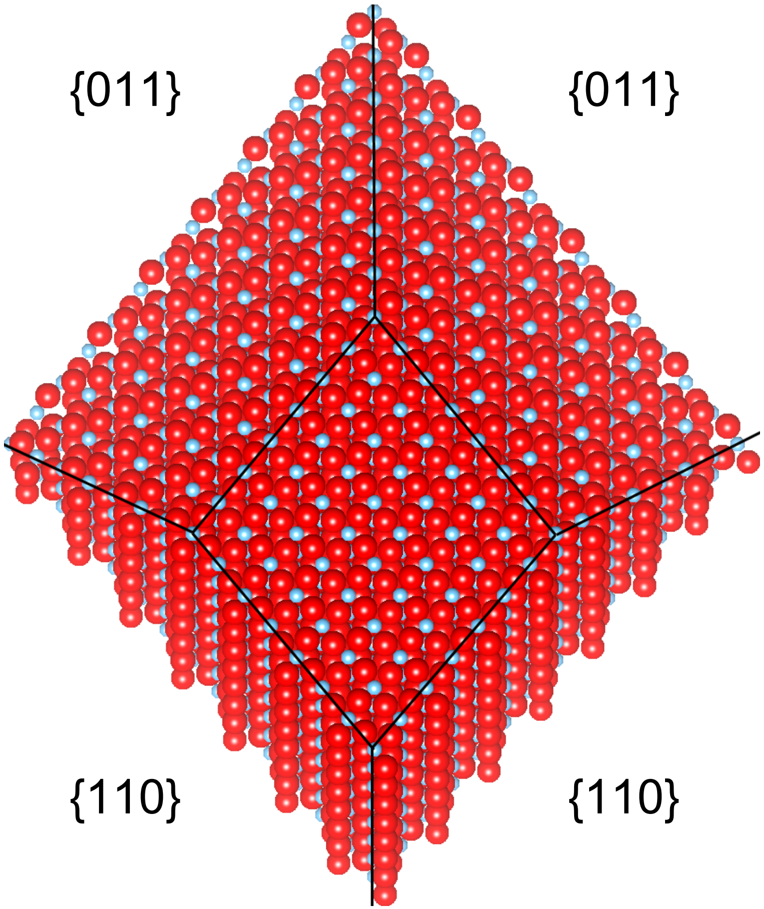


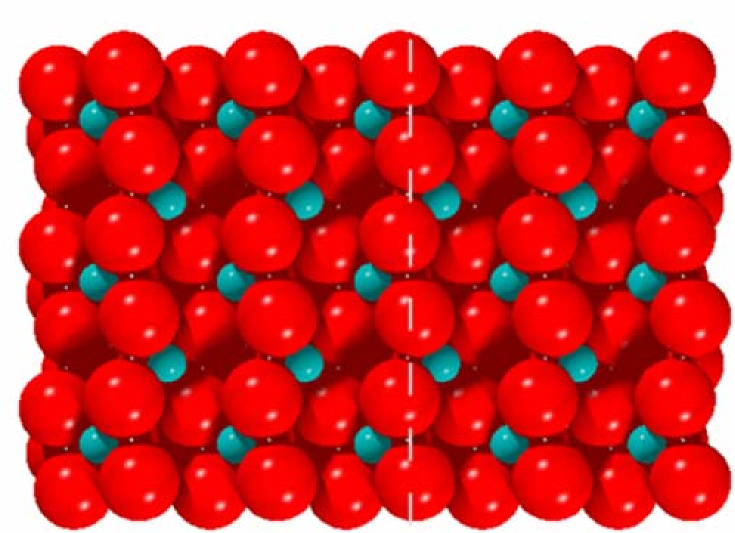


Ewald sphere construction with facets



Result of the experiment





Rutile(011)-(2x1) crystallites with facets according to the Wulff-construktion

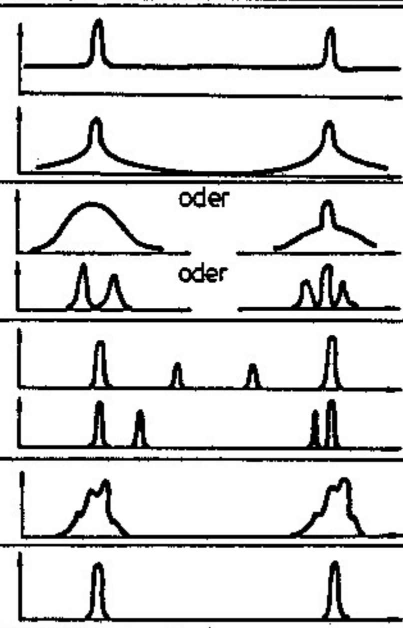
Glide line symmetry

LEED and defects

Information from spot shape (profile), background, E_0-dependence ($k_\perp$-dependence)

Nachweis von Oberflächendefekten mit Beugung

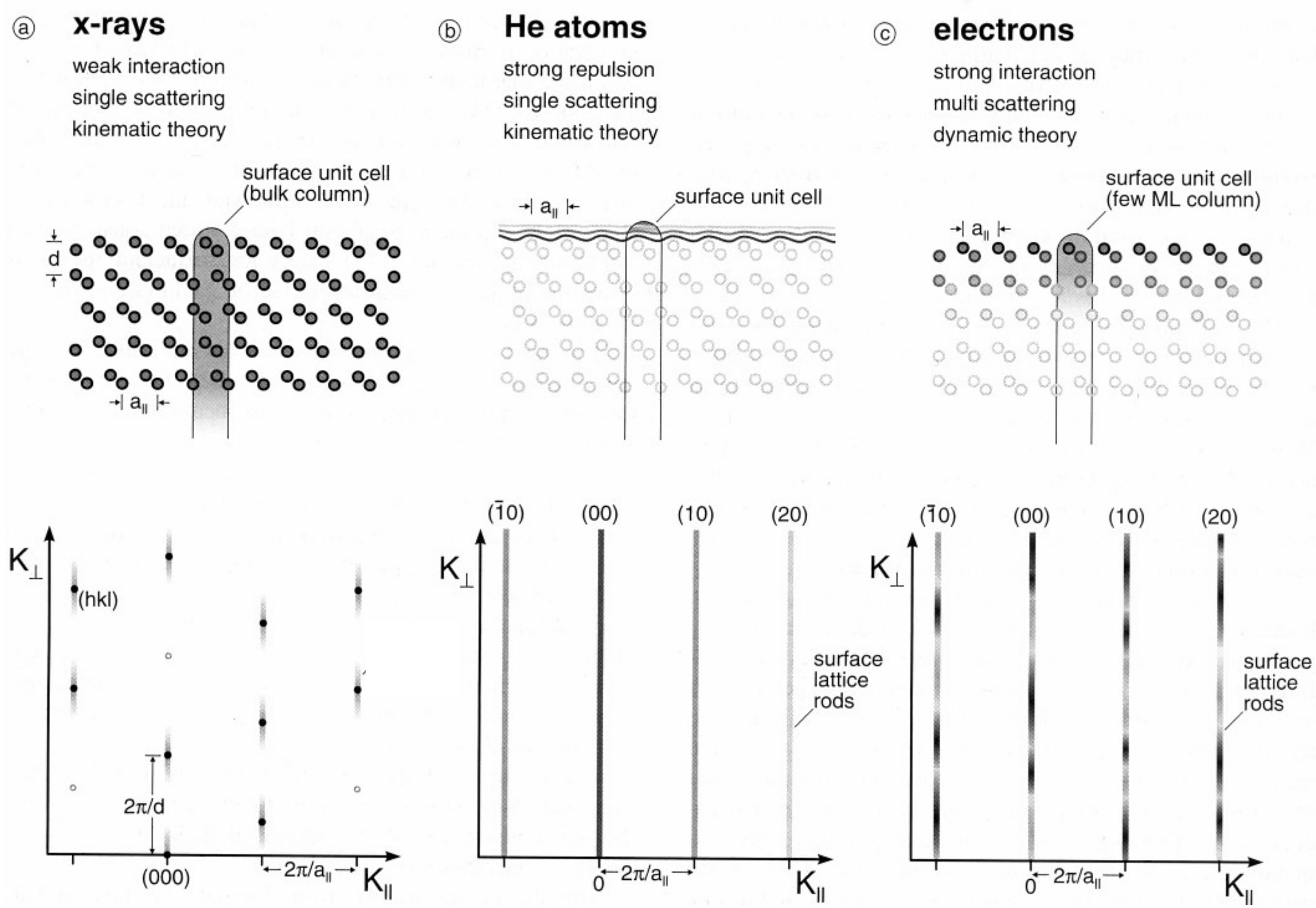
Dimension	Beispiele An	Einfluß auf Reflexprofil		$K_\perp$ Abhängigkeit
0	Punktfehler thermische Bewegung statische Unordnung	Anordnung: statistisch korreliert		keine
1	Stufenkanten Domänen (Größe, Grenzen)	statistisch regelmäßig	oder oder	periodisch (Stufen) keine (Domänen)
2	Überstruktur Facetten			keine periodisch
3	Volumendefekte (Mosaik, Verspannung)			monoton
ideale Oberflächen				keine



Henzler, Göpel Abb. 3.8.10, p.176

Special method: SPA-LEED (spot profile analysis), complementary to STM

Comparison with other methods



Surface diffraction with X-rays, He-atoms and electrons.
Example: diamond-type (111) surface like C, Si, Ge.
The darkness of rec. latt. spots and rods symbolizes diffraction intensity

Horn-von Hoegen, fig. 2.1

LEED – intensities

Spot intensities contain information on structure within the unit cell

$$I \sim |F|^2 \cdot |G|^2$$

$|G|^2$ = lattice factor

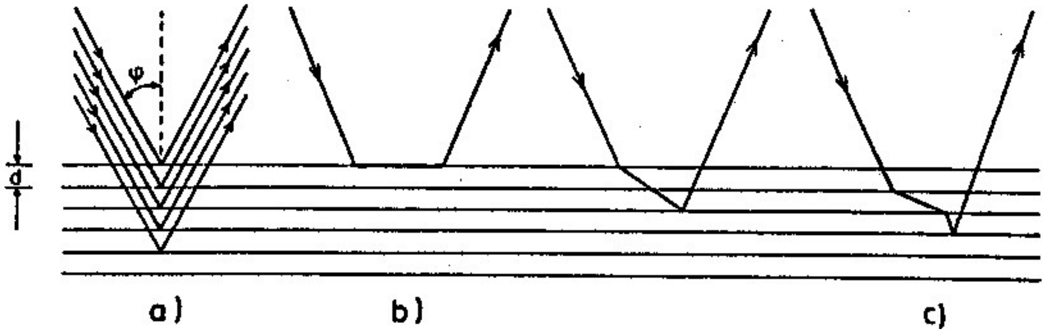
contains shape and arrangement of repeat units (unit cells)
yields reciprocal lattice
determines location and shape of spots,
kinematic theory

$|F|^2$ = structure factor or scattering factor

contains contribution from all atoms within the repeat unit,
includes multiple scattering, in-depth attenuation,
dynamic theory

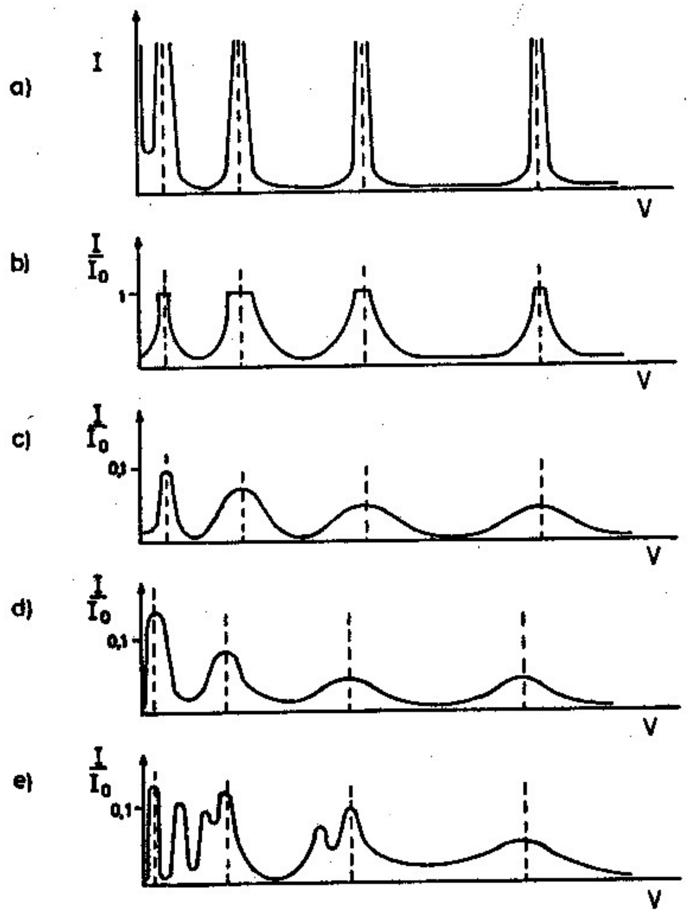
Multiple scattering

Henzler/Göpel fig. 3.7.3, p.151



LEED I-V measurement

I-V-curve (schem.)



Simple kinematic

with simple mult. scatt.

with damping

with inner potential

with complete mult. scatt.

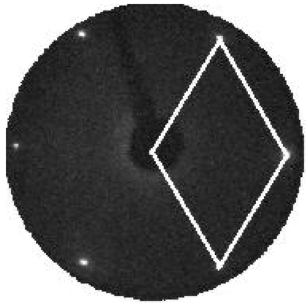
Henzler/Göpel, fig. 3.7.4, p.152

Dynamic LEED analysis:
No direct deduction of structure from I-V-curves:

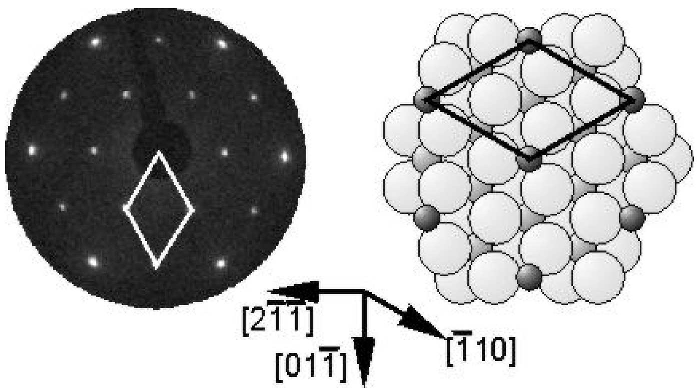
Guess structure model
calculate I-V-curves
compare with measured curves
modify model
check if improval
if yes: proceed modifying in this direction
if no: modify in another direction
or guess new model

Disadvantage:
Only for ordered structures
Much computer time

But:
One of very few methods for structure analysis of first few atomic layers (~1 nm)



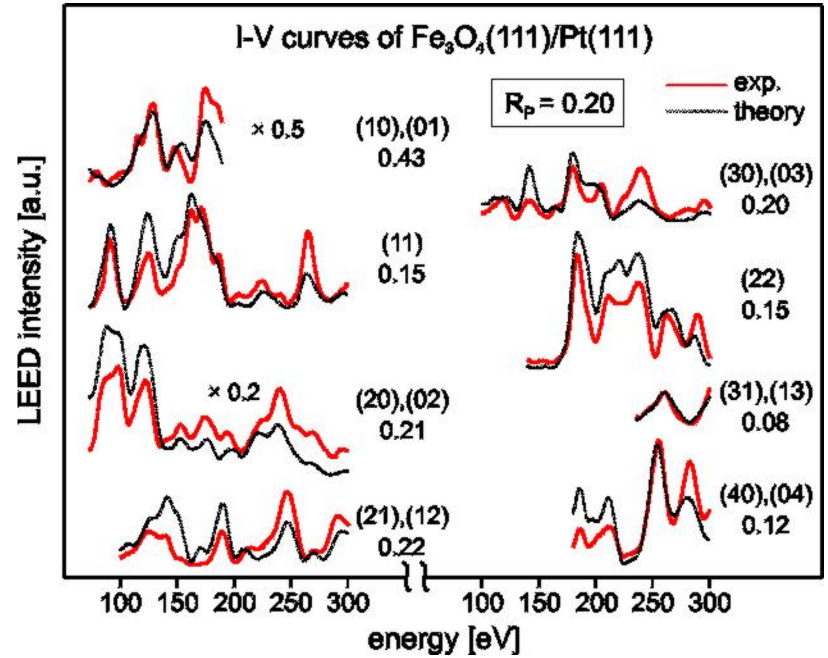
Pt(111)



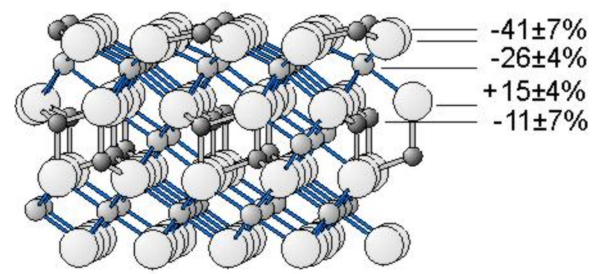
Fe_3O_4(111),
(inverse spinel)
10 nm thick
on Pt(111)

LEED-I-V analysis is one of very few reliable surface structure analysis methods!

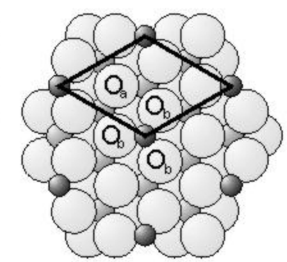
Michael Ritter,
Werner Weiss
Guido Ketteler



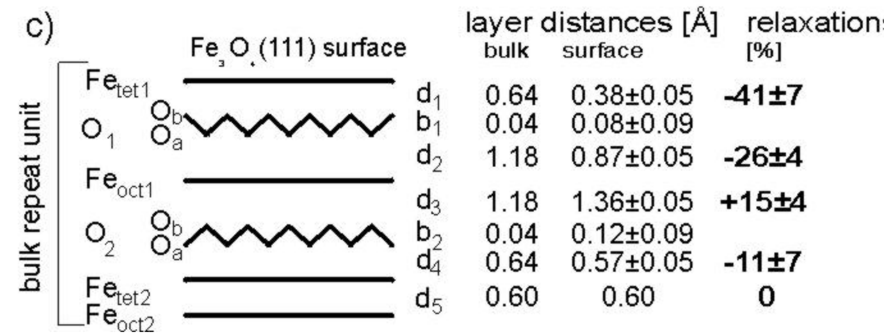
a)



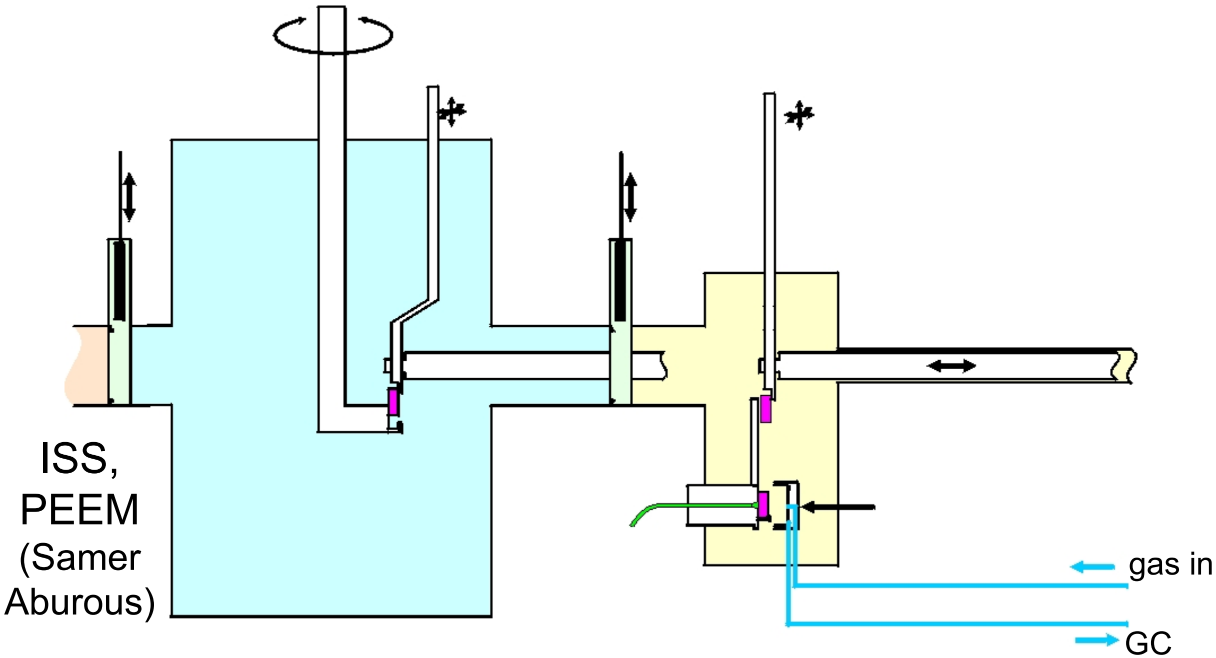
b)



c)

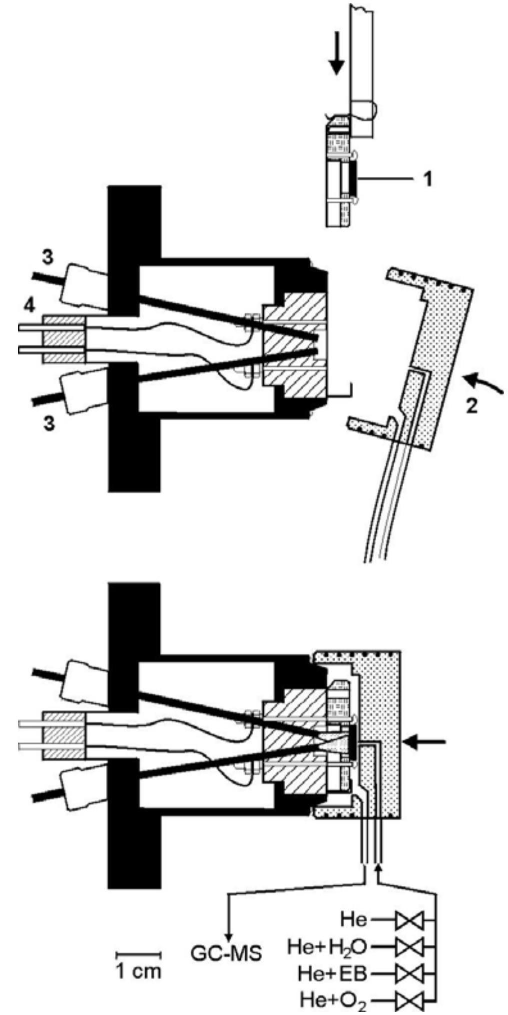


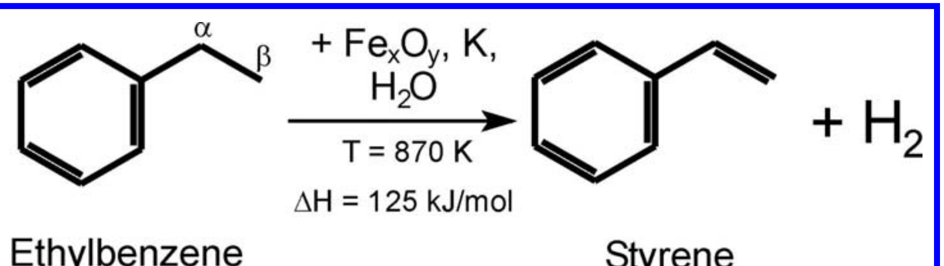
LEED in model catalysis - example



UHV
LEED, AES, TDS
p= 10^{-6} to
10^{-10} mbar

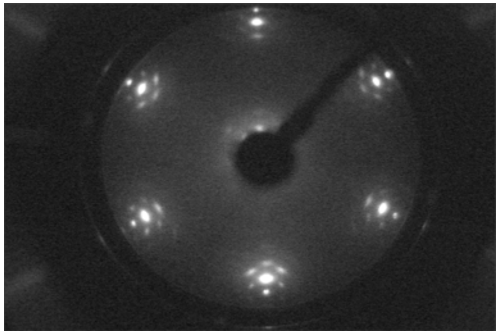
Preparation
reactor
p=1000 to
10^{-6} mbar



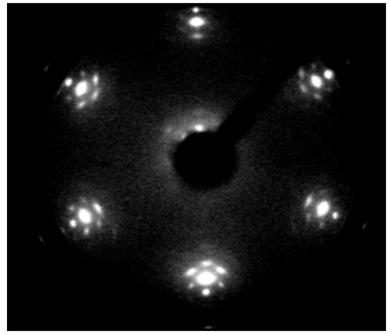


Manfred Swoboda
Christian Kuhrs
Werner Weiss

Distinguish different Fe-O-phases

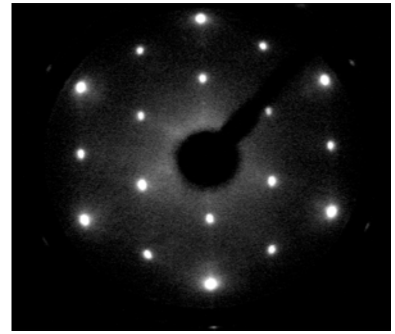


as measured

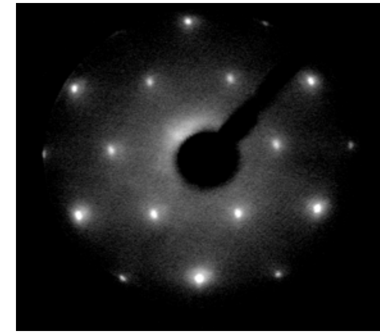


contrast enhanced

FeO(111)/Pt(111), 1 ML

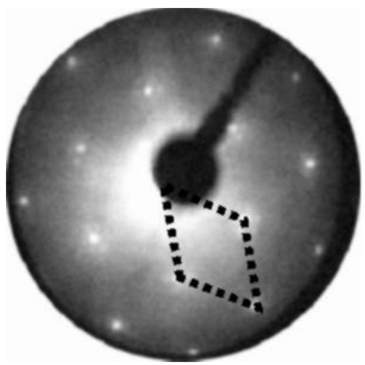


$Fe_3O_4(111)$

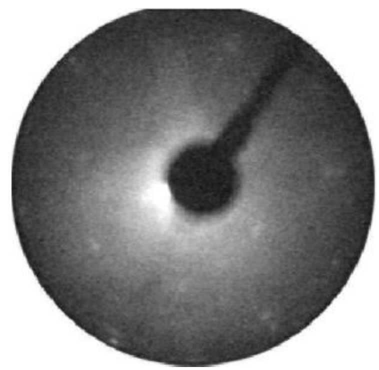


α-$Fe_2O_3(0001)$

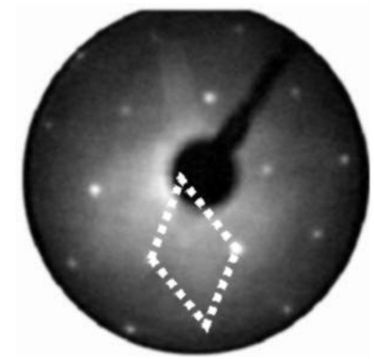
Change of order and phase during reaction



Starting surface:
α-$Fe_2O_3(0001)$
(hematite),
defective



After reaction
- no long-range order
- strong C peak in AES



After mild TPO
(thermal programmed oxidation)
- reordered
- no longer hematite but $Fe_3O_4(111)$ (magnetite

Osama Shekhah